TN 295
.U4

No. 8953

THE LIBRARY OF CONGRESS

IC 8953

Bureau of Mines Information Circular/1983

LIBRARY OF CONGRESS
4
NOV - 4 1983
COPY
EXCHANGE & GIFT DIVISION

Methods for Characterizing Manganese Nodules and Processing Wastes

By Benjamin W. Haynes, David C. Barron,
Gary W. Kramer, and Stephen L. Law

UNITED STATES DEPARTMENT OF THE INTERIOR

Information Circular 8953

Methods for Characterizing Manganese Nodules and Processing Wastes

By Benjamin W. Haynes, David C. Barron,
Gary W. Kramer, and Stephen L. Law

UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
Robert C. Horton, Director

TN295
.U4
no. 8953

Library of Congress Cataloging in Publication Data:

Methods for characterizing manganese nodules and processing wastes.

(Information circular / Bureau of Mines ; 8953)

Bibliography: p. 10.

Supt. of Docs. no.: I 28.27:8953.

1. Manganese nodules--Analysis. I. Haynes, Benjamin W. II. Series: Information circular (United States. Bureau of Mines) ; 8953.

~~TN295.U4~~ [QE390.2.M35] 622s [553.4'629'0287] 83-600240

CONTENTS

	Page
Abstract	1
Introduction	2
Physical methods	2
Compound identification methods	2
Chemical characteristics	4
Atomic absorption spectrophotometry	4
Inductively coupled plasma atomic emission spectroscopy	6
Neutron activation analysis	6
X-ray fluorescence spectrography	6
Ion chromatography	6
Wet chemical methods	7
Comparison of chemical analysis results	7
Leaching tests	8
EP toxicity test	8
ASTM shake extraction test	8
U.S. Army Corps of Engineers seawater elutriant test	9
Results of leaching tests	9
Conclusions	9
References	10

TABLES

1.	Suggested test procedures for determining physical properties of manganese nodule reject waste materials	3
2.	Physical properties of pilot plant- and laboratory-generated Cuprion process tailings	3
3.	Compound identification and elemental analysis methods for manganese nodule materials	3
4.	Sources of interference in elemental determination by quantitative instrumental methods	5
5.	Sample dissolution and elemental analysis procedures for manganese nodule materials	5
6.	Ion chromatograph operating conditions for determining anions and NH_4^+	7
7.	Comparison of interlaboratory analyses of manganese nodule standards	7
8.	Round-robin results for Cuprion process reject waste material, solid phase	8
9.	Round-robin results for Cuprion process reject waste material, liquid phase	8
10.	Element concentration in leachate from leaching tests on Cuprion process reject waste material	9

LIST OF UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm/s	centimeter per second	mL/min	milliliter per minute
deg	degree	mm	millimeter
°C	degree Celsius	min	minute
g	gram	nm	nanometer
h	hour	pct	percent
µg	microgram	pcf	pound per cubic foot
µg/mL	microgram per milliliter	psi	pound per square inch
µm	micrometer	wt pct	weight percent
mL	milliliter		

METHODS FOR CHARACTERIZING MANGANESE NODULES AND PROCESSING WASTES

By Benjamin W. Haynes,[1] David C. Barron,[2] Gary W. Kramer,[3] and Stephen L. Law[4]

ABSTRACT

Analytical procedures are described for the quantitative determination of 16 elements (As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn) and 7 ionic species (NH_4^+, CO_3^{2-}, Cl^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), identification of major and minor mineral components, and measurement of physical properties associated with manganese nodules and nodule processing reject waste materials.

Compound identification methods discussed include X-ray diffraction, infrared spectroscopy, scanning and transmission electron microscopy, selective area electron diffraction, and optical and reflected light microscopy. Methods for elemental analysis include atomic absorption spectrophotometry, inductively coupled plasma emission spectroscopy, neutron activation analysis, fluorescent X-ray spectrography, and ion chromatography. Thermal gravimetric analysis, ultraviolet-visible spectrophotometry, ion specific electrodes, and standard wet chemical procedures are briefly discussed.

Physical properties determined in manganese nodule materials include grain size distribution, specific gravity, triaxial shear, permeability, maximum density, Atterberg limits, and slurry density.

The results of a round-robin analysis of an ammonia process waste material and manganese nodule standards demonstrate the applicability of the discussed methods.

Tests discussed for the evaluation of the waste materials for disposal options include the Environmental Protection Agency (EPA) EP toxicity test, the ASTM shake extraction test, and the U.S. Army Corps of Engineers EPA seawater elutriant test.

[1]Supervisory research chemist.
[2]Chemist.
[3]Research chemist.
[4]Research supervisor.
Avondale Research Center, Bureau of Mines, Avondale, MD.

INTRODUCTION

Deep seabed mining for manganese nodules, including the processing of nodules to recover value metals, raises a variety of environmental, social, and economic considerations. To address the waste management aspects of the recovery of value metals from nodules, the National Oceanic and Atmospheric Administration (NOAA) of the Department of Commerce, the Environmental Protection Agency (EPA), and the Department of the Interior's Bureau of Mines and Fish and Wildlife Service, after consultation with industry, academia, and other concerned interests, entered a multiyear cooperative research program which has as its overall objective:

> "To provide information needed by Federal and State agencies in preparation for receipt of industry's commercial waste management plans."

The NOAA-funded research conducted by the Bureau of Mines has the objective of obtaining a "first-order chemical and physical characterization of rejects from the types of manganese nodule processing techniques representative of those being developed by industry." Three reports have been published since commencement of this research that delineate mineralogical and elemental composition of Pacific manganese nodules (*16*),[5] five potential process flowsheets for first-generation plants (*17*), and prediction of the compositions of the reject waste materials from the five potential processes (*15*) using information obtained in the first two reports. The five processes considered feasible for first-generation nodule processing are as follows (*7,17*):

1. Gas reduction and ammoniacal leach.
2. Cuprion ammoniacal leach.
3. High-temperature and high-pressure sulfuric acid leach.
4. Reduction and hydrochloric acid leach.
5. Smelting and sulfuric acid leach.

In order to assess any potential environmental impact of waste disposal from manganese nodule processing, accurate and precise analytical methods are essential. Because this industry is still in the developmental stage, actual waste materials are not available, and the direct applicability of commonly used analytical methods was uncertain. The combination of high manganese and high iron content is unique to these materials, and interferences will result in incorrect data unless precautions are taken.

This report outlines methods that Bureau of Mines experience has indicated are applicable to the characterization of nodule feed materials and the reject waste materials from all five potential processes. The report is divided into five sections: methods for determining physical properties, methods for compound identification, methods for determining chemical characteristics, interlaboratory comparisons of results, and leach tests for hazardous waste and ocean disposal assessment.

The chemical characteristics section discusses the determination of elements of potential economic and/or environmental interest and anion or cation combining species. Elements of interest are As, Ba, Be, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn (*15*). Silver and mercury are not specifically addressed in this report as their levels in nodules are too low to warrant environmental concern (*15-16*). Ions of interest include ammonium, carbonate, chloride, flouride, nitrate, phosphate, and sulfate.

The various methodologies for testing physical properties incorporate standard ASTM and soil mechanics procedures. Analysis of liquid and solid phase components for chemical characteristics involve the use of atomic absorption spectrophotometry (AAS), inductively coupled plasma spectroscopy (ICP), ion chromatography (IC), X-ray fluorescence (XRF), X-ray diffraction (XRD), and/or wet chemical procedures. Parameters such as pH, reduction-oxidation potential, and chemical oxygen demand may also need to be determined. Modifications of these basic methods and the use of other methods may be required for specific needs of different laboratories.

The procedures and methods presented in this report are not to be considered as proposed standard methods or as the only methods suitable for characterization of these types of materials. Attention has been given to methods that are capable of multielement analysis, thereby reducing the amount of sample and the time required for analyses.

PHYSICAL METHODS

Physical characteristics are determined by the application of ASTM methods outlined for soils and rock testing (*3*). The test procedures listed in table 1 have been successfully applied to coal refuse by the Bureau of Mines (*6*). The same test procedures were used to determine the physical characteristics of tailings generated in pilot-plant and laboratory operations, and the results are presented in table 2. The agreement between results of the two types of tailings in table 2 demonstrates the ability to simulate the pilot-plant physical characteristics on the laboratory scale. However, these results may not be typical of tailings that may be produced in a full-scale plant because optimization of all processing parameters is not achievable on a pilot-plant or laboratory scale.

COMPOUND IDENTIFICATION METHODS

Identification of the various compounds present in nodule reject waste materials allows a preliminary evaluation of the wastes' environmental impact. An element present in one chemical form may be environmentally inert, whereas a more chemically active form of the element may pose problems if disposed of improperly. However, this identification is inherently difficult because of the poorly crystalline, fine-grained, or amorphous nature of the minerals in manganese nodules and their tailings. Methods, such as XRD, optical microscopy, infrared spectroscopy, thermal analysis, and scanning and transmission electron microscopy, are available to identify

[5]Italicized numbers in parentheses refer to items in the list of references at the end of this report.

Table 1.—Suggested test procedures for determining physical properties of manganese nodule reject waste materials

Property	Procedure[1]
Grain size distributions:	
Plus 200 mesh	ASTM D422-63.
Minus 200 mesh	Allen *(1)*.
Specific gravity	ASTM D854-58.
Triaxial shear	ASTM D2850-70.
Permeability	ASTM D2434-68.[2]
Maximum density	ASTM D698-78.
Minimum density	ASTM D2049-69.
Atterberg limits:	
Liquid	ASTM D423-66.
Plastic	ASTM D424-59
Soil class	ASTM D2487-69.
Slurry density	ASTM D2216-71.

[1] ASTM tests are found in reference 3.
[2] Using Bureau of Reclamation Earth Manual Procedure E13.

Table 2.—Physical properties of pilot plant- and laboratory-generated Cuprion process tailings

Parameter	Pilot plant	Laboratory
Grain size distribution, μm:		
100 pct pass	74	600
50 pct pass	6	13
0 pct pass	1	1
Specific gravity	[1] 3.19	3.10
Triaxial shear:		
Friction angle, deg	38	38.5
Cohesion, psi	5	4
Permeability[2], 10^{-6} cm/s	8.46	6.7
Maximum density, pcf	90.1	92.5
Atterberg limits:		
Liquid, pct	45	42.1
Plastic, pct	41.2	34.4
Soil class	[3] ML	[3] ML
Slurry density, pct solids	41.8	31.1

[1] Dry solids. [2] At 95 pct maximum density. [3] Lean silt.

major and minor compounds. Table 3 includes a brief sketch of each of these methods along with the methods primarily used for elemental and anion determinations discussed in the next section.

XRD is the conventional technique used to identify and sometimes quantify major and minor crystalline compounds. However, in the iron and manganese matrix of manganese nodules, compounds that are present at less than 5 wt pct and/or are extremely fine grained, generally cannot be identified by this method. Many of the minerals present in nodules (*16*) are very poorly crystalline, and often amorphous, given only a diffuse XRD pattern. The reject waste materials from manganese nodule processing are also relatively fine grained but do show better crystallinity and thus better diffraction patterns than nodules. The major and minor components such as manganese carbonate, manganese oxides, silica, clays, and feldspars can be determined. Positive association of trace elements with specific compounds is virtually impossible by this method.

Identification of compounds in single grains requires the use of the transmission electron microscope (TEM) using selective area electron diffraction (SAED) (*30*). This technique uses very small samples and applies to single particles. Quantification on this scale is impractical because of the lack of appropriate standards for manganese nodule materials.

Infrared spectroscopy (IR) is useful for the mineralogical analyses of manganese nodules, which cannot be performed by XRD (*22-23*). For example, it eliminates the ambiguity frequently caused in XRD by silicate components, such as the confusion of kaolinite and birnessite (*23*). Being sensitive to short-range order, IR provides mineralogical information on the disordered and fine-particulate phases that cannot be studied by XRD (*22*). However, because IR is not a primary structural technique like XRD, it is necessary to calibrate it

Table 3.—Compound identification and elemental analysis methods for manganese nodule materials

Atomic absorption spectroscopy:
- **Application**—Quantitative determination of a specific element, especially minor and trace concentrations.
- **Principle**—Absorption of atomic resonance line proportional to the concentration of the specific element.
- **Limitations**—Usually not applicable to nonmetals. Metals are determined individually and not simultaneously.

Atomic emission spectroscopy:
- **Application**—General qualitative and semiquantitative survey of all metallic elements.
- **Principle**—Light emission from excited electronic states of atoms proportional to concentration.
- **Limitation**—Poor for detecting volatile elements. Quantitative determinations are difficult.

Chemical reaction methods (classical analysis):
- **Application**—Variety of specialized quantitative applications.
- **Principle**—Stoichiometry of chemical reactions.
- **Limitations**—Time consuming, interferences often a problem.

Electron microscopy and microanalysis (SEM, TEM, and probe):
- **Application**—Morphological information and elemental composition of fine particles.
- **Principle**—A focused beam of electrons gives rise to secondary, backscattered, reflected, or transmitted electrons for morphological information, and X-rays for elemental information.
- **Limitations**—Sample must be small enough to fit in the sample chamber. Less than about 6-mm square maximum area is viewed by SEM, less than 1.5-mm square area for TEM, and about 50-mm square area for an electron probe.

Inductively coupled plasma:
- **Application**—Minor, trace and ultratrace quantitative and semiquantitative element analysis including B, P, and S, with linearity often over 4 orders of magnitude.
- **Principle**—Characteristic emissions from elements excited by an inductively coupled argon plasma have intensities proportional to concentrations.
- **Limitations**—Some spectral and scattered light interferences may come from the high concentrations of Fe and Mn in nodules.

Ion chromatography:
- **Application**—Rapid quantitative determination of anions. Rapid cation determination for alkali and alkaline earth metals, NH_4^+ and 1st row transition elements.
- **Principle**—Ions separated by ion exchange techniques followed by ion electrical conductance proportional to the concentration of the specific ion.
- **Limitations**—Usually not applicable to anions with pKa >7. Most 2d and 3d row cations are determined with difficulty.

Infrared spectroscopy:
- **Application**—Identification of compounds, amorphous and crystalline.
- **Principle**—Excitation of molecular vibrations by light absorption.
- **Limitations**—Medium sensitivity down to 1 to 2 pct. Broad absorption bands of OH group may overlap other spectral features in application to nodules.

Neutron activation:
- **Application**—Trace and ultratrace elemental analysis of most elements including N, O, and F.
- **Principle**—Counting of radioactive species produced by neutron reactions.
- **Limitations**—The multielement nature of nodules present problems in spectral overlaps, which require chemical separation for some elements.

Table 3.—Compound identification and elemental analysis methods for manganese nodule materials—Continued

Optical microscopy:

Application—Mineral or phase identification.
Principle—Properties such as color, cleavage, refractive index, and characteristic crystal shapes using plane and polarized, transmitted, and reflected light systems.
Limitations—Resolution limit is about 0.2 μm but identification of particles <5 μm is not practical, limiting the use of this technique for fine-grained nodule materials.

Thermal analysis (TGA and DTA):

Application—Qualitative and quantitative studies of materials including phase transitions, dehydration, reduction decomposition, crystallization, oxidation, and other heat-related properties.
Principle—Changes in weight are measured as a function of increased temperature over time.
Limitations—Information is often empirical, and complementary analytical methods are needed to properly interpret data.

Ultraviolet-visible spectrophotometry:

Application—Quantitative analysis usually for final determination in chemical analysis schemes.
Principle—Excitation of loosely bonded electrons with absorption of characteristic wavelength being proportional to the concentration of the compound.
Limitations—Low specificity requiring chemical separation procedures prior to final determination.

X-ray diffraction:

Application—Identification of crystalline substances.
Principle—Diffraction of X-rays from crystal planes providing "fingerprint" identification of crystalline materials.
Limitations—Many nodule minerals are too fine grained or amorphous, making X-ray diffraction inapplicable. Generally not useful in the atomic number matrix of nodules for concentrations <5 wt pct.

X-ray fluorescence spectrography:

Application—Quantitative analysis of elements and semiquantitative survey of all elements of atomic number 11 or greater.
Principle—X-ray excitation of characteristic X-rays.
Limitations—Nonsensitive to elements of atomic numbers <11 (Na). Best sensitivity for heavier atomic number elements.

against well-crystallized materials where mineralogy has been previously determined by XRD. Similar to XRD, direct IR is limited to compounds present at 2 to 5 pct or more in the sample. Other methods of compound identification such as optical microscopy, visual inspection, reflectivity, and other chemical and physical methods have definite applications. A combination of procedures is usually important to obtain reliable compound identification on the macrocrystalline and microcrystalline scale. A detailed description of over 50 minerals identified in manganese nodules is given in reference 16.

CHEMICAL CHARACTERISTICS

Elemental determination in manganese nodule processing reject waste material is amenable to several standard analytical methods. (See table 3.) Interferences for 16 elements of interest in manganese nodule materials are listed in table 4 for four major instrumental analysis methods. Because of their importance in the determination of element concentrations in nodule materials, a brief discussion of each instrumental method listed in table 4 is given, followed by a brief discussion of ion chromatography for the determination of ions.

ATOMIC ABSORPTION SPECTROPHOTOMETRY

Atomic absorption spectrophotometric (AAS) techniques are readily adaptable for analysis of both the solid and liquid phases (*15*). In the liquid phase, direct flame, electrothermal, and hydride methods of AAS are applicable depending on the element and the concentration levels. Most elements are readily determined by flame AAS, but may require the use of electrothermal AAS if the levels are below flame AAS detection limits. For As, Sb, and Se, either hydride or electrothermal AAS should be used. Specific methods or the use of a standard addition method may be required for some elements (*24*). Instrumental parameters and conditions for determining these elements can be found in the EPA manual, "Methods for Chemical Analysis of Water and Wastes" (*32*).

For solid phase analysis (nodules or tailings), several multielement dissolution procedures are available. This report will address only three simple, rapid dissolution procedures. One method is used for the determination of the seven major and minor elements (Mn, Fe, Cu, Ni, Co, Pb, and Zn) and several trace elements (Cr, Tl, Cd, and Ba) by flame AAS. The other two dissolution procedures are used for determining trace elements by either electrothermal or hydride AAS.

The dissolution procedure for determining the major, minor, and some trace elements in nodules and in the solid phase of the reject waste material uses HCl-HF acids with the resultant solution evaporated to dryness. This dried residue is then dissolved in 6*N* HCl, diluted to volume, and analyzed by flame AAS.

Determination of the trace elements As, Sb, and Se by electrothermal or hydride AAS requires a separate dissolution procedure (*13*) to avoid analyte loss of the volatile compounds formed during evaporation of the solution and during the drying and charring stages prior to electrothermal atomization. The sample is dissolved in a HNO_3-HF mixture with the addition of $Ni(NO_3)_2$ and $Mg(NO_3)_2$ as matrix modifiers. Additional trace elements that can be determined by electrothermal AAS are Ba, Cd, Cr, and Pb.

High iron levels cause a spectral interference at the primary selenium wavelength of 196.0 nm (*21*). This spectral overlap problem can be solved by adjusting the pH of the solution to 3 to 4 to precipitate the iron, with the selenium quantitatively carried on the $Fe(OH)_3$ precipitate. This precipitate is separated and redissolved in 7*N* HCl and the solutions are analyzed by hydride AAS to determine selenium.

The selenium forms a hydride whereas iron does not react and therefore does not interfere. The use of polarized Zeeman-effect AAS on the original solution is a more direct way to eliminate the spectral interference caused by iron (*19*). This technique uses the magnetic portions of the selenium analytical line, which facilitates the instrumental separation of iron and selenium spectral lines.

A third dissolution procedure for the analysis of nodules and solid phase reject materials is a Parr[6] bomb dissolution with aqua-regia-HF acid (*28*). All 16 elements are solubilized without loss and can be determined using flame AAS for the major and minor elements, and the remaining trace elements can be determined by flame, hydride, or electrothermal AAS. In deter-

[6]Reference to specific products does not imply endorsement by the Bureau of Mines.

Table 4.—Sources of interference in elemental determination by quantitative instrumental methods

Arsenic:
- AAS . . . . . High Fe, Mn, and other metals will depress the sensitivity in hydride generation. Flame method gives poor sensitivity.
- ICP . . . . . 2d-order spectral overlap from Ar.
- NAA . . . . . Interference from Se, Ge, and Br.
- XRF . . . . . Pb spectral interference at more sensitive Kα peak. Kβ peak lacks sensitivity for quantities below 0.02 pct.

Barium:
- AAS . . . . . Ionization controlled by adding KCl. CaOH bands interfere.
- ICP . . . . . None reported.
- NAA . . . . . Interference from Ce and La.
- XRF . . . . . None reported for quantities above 0.05 pct.

Beryllium:
- AAS . . . . . High Al, Mg, and Si will depress sensitivity.
- ICP . . . . . 2d-order spectral overlap from Ar and OH band interference.
- NAA . . . . . Not recommended.
- XRF . . . . . Atomic number too low for XRF.

Cadmium:
- AAS . . . . . High Si interferes.
- ICP . . . . . None reported.
- NAA . . . . . Interference from Sn and from shielding.
- XRF . . . . . None reported for quantities above 0.02 pct.

Cobalt:
- AAS . . . . . Some heavy metals and transition metals depress signal.
- ICP . . . . . 2d-order spectral overlap from Ar.
- NAA . . . . . Ni, Cu, and Fe cause enhancements.
- XRF . . . . . Fe spectral interference below 0.01 pct.

Chromium:
- AAS . . . . . Fe, Ni, and PO_4^{3-} depress the signal.
- ICP . . . . . OH band interference.
- NAA . . . . . Interference from Fe.
- XRF . . . . . Enhanced by high iron.

Copper:
- AAS . . . . . None reported.
- ICP . . . . . 2d-order spectral overlap from Ar.
- NAA . . . . . Interference from Ni and Zn.
- XRF . . . . . None reported for quantities above 0.005 pct.

Iron:
- AAS . . . . . Co, Cu, Ni, Si, and organic acids depress signal.
- ICP . . . . . None reported.
- NAA . . . . . Poor detectability from Co, Cr, Mn, and Ni.
- XRF . . . . . None reported for quantities above 0.005 pct.

Manganese:
- AAS . . . . . Si depresses signal. High concentration of Fe enhances signal.
- ICP . . . . . 2d-order spectral overlap from Ar and OH band interference.
- NAA . . . . . Interference from Fe, Co, and Cr.
- XRF . . . . . None reported for quantities above 0.005 pct.

Molybdenum:
- AAS . . . . . Cu, Fe, Sr, and SO_4^{2-} depress the signal.
- ICP . . . . . OH band interference.
- NAA . . . . . Interference from Ru.
- XRF . . . . . None reported for quantities above 0.02 pct.

Nickel:
- AAS . . . . . High Fe or Cr will enhance signal.
- ICP . . . . . 1st order spectral overlap from Si.
- NAA . . . . . Interference from Cu and Zn for Ni-64. No apparent interference for Ni-58.
- XRF . . . . . None reported for quantities above 0.005 pct.

Lead:
- AAS . . . . . High Fe or other metals will enhance the signal.
- ICP . . . . . 2d-order spectral overlap from H.
- NAA . . . . . Interference from Bi.
- XRF . . . . . None reported for quantities above 0.01 pct.

Antimony:
- AAS . . . . . Spectral interference from Cu and Pb. Depressed signal in high acidity.
- ICP . . . . . 1st order spectral overlap from Si and 2d-order overlap from Ar.
- NAA . . . . . Interference from Te and from self-shielding.
- XRF . . . . . None reported for quantities above 0.02 pct.

Selenium:
- AAS . . . . . Some metals will depress the hydride generation signal. Flame absorbs signal.
- ICP . . . . . None reported.
- NAA . . . . . Interference from Ge and Br.
- XRF . . . . . None reported for quantities above 0.01 pct.

Thallium:
- AAS . . . . . None reported.
- ICP . . . . . 1st order spectral overlap from Ar.
- NAA . . . . . Interference from Pb and Hg.
- XRF . . . . . None reported for quantities above 0.02 pct.

Zinc:
- AAS . . . . . High Cu, Fe, and Ni depress signal.
- ICP . . . . . None reported.
- NAA . . . . . Interference from Cu and Ni.
- XRF . . . . . None reported for quantities above 0.005 pct.

AAS Atomic adsorption spectrophotometry.
ICP Inductively coupled plasma.
NAA Neutron activation analysis.
XRF X-ray diffraction.

mining As, Sb, and Se by electrothermal AAS, matrix modifiers must be added to prevent losses during the drying and charring stages prior to atomization (*13*).

Table 5 identifies each of the major elements as a major, minor, or trace component in manganese nodules, and gives suggested dissolution procedures and applicable methods for determination. For flame AAS conditions, relative error is generally 2 to 5 pct of the actual value. At the very low levels determined by hydride or electrothermal AAS, the relative error is within 5 to 7 pct of the actual value.

Table 5.—Sample dissolution and elemental analysis procedures for manganese nodule materials

Element	Concentration	Dissolution procedure[1]	Method of analysis[2]	Element	Concentration	Dissolution procedure[1]	Method of analysis[2]
As	Trace	HNO_3-$Ni(NO_3)_2$	Hydride or electrothermal AAS.	Fe	Major	HCl-HF	Flame AAS.
				Mn	...do.	HCl-HF	Do.
Ba	Minor	HCl-HF; HNO_3-$Ni(NO_3)_2$.	Flame or electrothermal AAS.	Mo	Minor	HCl-HF	Do.
				Ni	Major	HCl-HF	Do.
Be	Trace	HCl-HF; HNO_3-$Ni(NO_3)_2$.	Do.	Pb	Minor	HCl-HF; HNO_3-$Ni(NO_3)_2$.	Flame or electrothermal AAS.
Cd	...do.	HCl-HF; HNO_3-$Ni(NO_3)_2$.	Do.	Sb	Trace	HNO_3-$Ni(NO_3)_2$	Hydride or electrothermal AAS.
Co	Minor	HCl-HF	Flame AAS.	Se	...do.	HNO_3-$Ni(NO_3)_2$	Do.
Cr	Trace	HCl-HF; HNO_3-$Ni(NO_3)_2$.	Flame or electrothermal AAS.	Tl	...do.	HCl-HF	Flame AAS.
				Zn	Minor	HCl-HF	Do.
Cu	Major	HCl-HF	Flame AAS.				

[1] The Parr bomb dissolution procedure is suitable for all 16 elements.
[2] Inductively coupled plasma atomic emission spectroscopy is suitable for all 16 elements.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

The same sample preparation techniques used for atomic absorption are used for preparing solutions for the inductively coupled plasma (ICP) technique for multielement analysis by atomic emission spectroscopy. Atomic emission lends itself more readily to multielement analysis than does atomic absorption, and the interelement effects, self-absorption problems, and poor excitation of refractory elements, which create problems in conventional atomic emission spectroscopy, are greatly reduced in ICP. Spectral and interelement interferences are a basic problem in any emission technique; however, interferences from background emission, flame gases, combustion products, and molecular species are greatly reduced in ICP. The few interferences that may cause problems in the analyses of manganese nodule materials are listed in table 4. The relative error in determining major, minor, and trace elements in nodule materials by ICP is slightly higher compared with the 2 to 5 pct cited for AAS in the previous section.

NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis (NAA) can provide concentration values, especially on a trace level (<0.001 pct), which might otherwise be impractical. However, a number of interferences (*18, 25*) may create problems in measuring specific activities (see table 4).

With materials such as manganese nodules, sensitivity and accuracy can be obtained in the measurement of the radioactive products from most of the elements only after chemical separation. The major types of counting interferences include the masking of trace element activities by the much greater activities of one or more other elements because of amounts, cross sections, or long half-lives, and the occurence of similar gamma-ray photopeaks or β^- emissions that are not conveniently resolved (for example, Fe-59 and Co-60). Postirradiation separations are preferred over preirradiation because no reagent blank is involved and the postirradiation separation need not be quantitative in many cases to obtain quantitative results. The chemical separations, whether performed before or after irradiation, follow conventional methods except for added precautions in working with the radioactive samples. A procedure using chemical separations for the determination of 42 elements in lunar material (*5*) would appear to require very little modification to provide good results for manganese nodule materials.

X-RAY FLUORESCENCE SPECTROGRAPHY

The application of X-ray fluorescence (XRF) spectrography to manganese nodule and reject waste materials involves conventional methods of XRF analysis with corrections for peak overlap and enhancement and depression effects. The wavelength- and energy-dispersive methods of XRF are applicable for Co, Cu, Fe, Mn, Ni, Zn, and Pb where these elements are major or minor constituents of the solid phase (nodules or tailings). The remaining elements of interest for this report are at levels not usually detectable by direct XRF methods. A good general reference on XRF analysis is Bertin (*4*).

Sample preparation of nodules or tailings for XRF analysis requires drying to remove moisture, followed by one of two methods of sample preparation: pressed pellets or fused disks. To prepare pressed pellets, the dry weighed sample is mixed with a binder and pressed into a pellet at ~15 tons per square inch pressure. These pellets are then analyzed and compared with standards of known composition for the elements of interest. The second sample preparation procedure, fused disks, requires a dry weighed sample to be mixed with a glass-forming low-atomic number material, followed by fusion at high temperature (~ 800°-1,200° C). This method eliminates particle size problems and reduces matrix effects. However, sensitivity is decreased because of dilution of the sample by the glass-forming material. The dilution is usually about six parts flux to one part sample in fusions compared with pressed pellets where 85 pct of the final pellet is sample. This loss of sensitivity by using fused disks may pose a problem if concentrations of the element of interest are already low.

Major and minor elements can be determined by XRF provided that adequate primary and secondary standards can be obtained and/or made for the elements of interest in an appropriate matrix. The precision of analysis will vary from ±1 pct of the amount present for the major elements (>5 pct) such as manganese and iron, and ranges up to ±20 pct of the concentration present for elements in the very low (<0.1 pct) range. This relative error is also very dependent on atomic number in the lower concentration range, with the greater problems occurring with the lower atomic number elements. Applications of XRF to nodule analysis has been reported (*10, 12*), giving X-ray values in good agreement with atomic absorption analyses of nodules (*11*).

ION CHROMATOGRAPHY

Conventional, standard wet chemical, and colorimetric methods for chloride, fluoride, nitrate, ammonium, phosphate, and sulfate are available (*32*). In order to determine five anions of interest in the manganese nodule materials using the conventional methods, a separate sample would be required for each anion determination. Since the introduction of ion chromatography (IC) (*29*), this multi-ion method has been used to determine many anions and cations in a variety of environmental and geological matrices (*14, 20, 26-27*).

In the liquid phases from processing nodules, NH_4^+, Cl^-, SO_4^{2-}, and CO_3^{2-} can be determined by sample dilution followed by injection into the IC. Table 6 summarizes the operating conditions for determining six anions and one cation of interest. The six anions, F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, and CO_3^{2-} can be determined in less than 20 min on one sample using one set of conditions. The ammonium ion can be determined in a separate sample of the liquid fraction using another set of IC conditions (*20*).

For liquid samples, IC methods for determining carbonate (CO_3^{2-}) depend on concentration. At >500-µg/mL levels, the parameters outlined in table 6 are adequate. For <500-µg/mL levels, a separate method, called ion exclusion is required. In ion exclusion only a suppressor column is required and distilled water is used as the eluent; this procedure is applicable down to the 1-µg/mL level.

Transition metal ions such as Fe^{3+} tie up active sites in the resins used in IC, effectively "poisoning" the resin. This problem is resolved by inserting a small precolumn in the system. The transition ions remain in the precolumn without affecting the separator's column efficiency. The precolumn is periodically replaced to prevent carryover to the separator column.

Acid dissolution of solids is not practical because the acid or combination of acids used in the dissolution will prevent the determination of the acid anions in the original sample. By fusing the sample with Na_2CO_3 and leaching with deionized water, the anions in the sample are converted to the water

Table 6.—Ion chromatograph operating conditions for determining anions and NH_4^+

Constituent	Elution time[1] min	Possible interferences	Detection limits, μg/mL
Chloride (Cl^-)	≈4	High CO_3^{2-} (>1,000 μg/mL).	0.5
Fluoride (F^-)	≈1.5	None expected	.2
Nitrate (NO_3^-)	≈9	High PO_4^{3-} (>100 μg/mL).	1.0
Phosphate (PO_4^{3-})	≈7	High NO_3^- (>100 μg/mL).	1.0
Sulfate (SO_4^{2-})	≈15	None expected	1.0
Carbonate (CO_3^{2-})	≈3	High Cl^- (>50 μg/mL).	[2]500.0
Ammonium (NH_4^+)	≈16	High Na (>100 μg/mL).	5.0

[1] All elution times are based on using a 0.003*M* $NaHCO_3$/0.0024*M* Na_2CO_3 eluent and a 3- by 500-mm anion separator column for all except ammonium (0.005*M* HNO_3 eluent and a 6- by 250-mm cation separator) at a flow rate of 2.5 mL/min.

[2] A limit of ~1 μg/mL can be detected by use of ion exclusion using distilled H_2O as an eluent and the suppressor column only.

soluble Na^+ form. This fusion technique has the additional advantage of forming transition metal carbonates that generally remain insoluble, thereby eliminating the transition metal poisoning of the column. After the samples are fused and water leached, the liquid is injected into the IC for analysis. A Bureau of Mines developed fusion technique was applied successfully to the anion IC characterization of phosphate minerals (*14*) and cement kiln dust (*20*).

The carbonate ion in the solid phase cannot be analyzed by IC using the fusion method because of the CO_3^{2-} contribution from the flux. Thermal gravimetric analysis of the unfused solid allows the determination of CO_3^{2-} concentration based on the thermal evolution of CO_2 coupled with gas chromatograpy. The evolution of CO_2 by acid with subsequent capture of CO_2 could also be applicable.

Detection limits for the various ions by IC are given in table 6. The IC method is generally within ±5 pct relative of the actual value depending on the concentration of the ions of interest.

WET CHEMICAL METHODS

Classical wet chemical methods of analysis are available for use in determining individual elements and ionic species of interest, but they are generally time consuming and require a separate sample for each determination. Various standard analytical methods are listed by EPA (*32*) including titrimetric, gravimetric, spectrophotometric, potentiometric, and specific ion electrode methods in addition to specific parameter methods such as chemical oxygen demand (COD) and pH. The focus of this report is on the use of multielement techniques however, and no detailed discussion will be made of these single constituent analytical methods.

COMPARISON OF CHEMICAL ANALYSIS RESULTS

Several nodule materials were used for interlaboratory comparisons of analytical methods. Seven manganese nodule standards were received, five were in-house standards from two industrial laboratories (A and B) and the other two were available from the U.S. Geological Survey (USGS) (*11*). Analytical results from laboratories A and B and the two USGS standards are compared with results obtained by the Bureau's Avondale (MD) Research Center in table 7.

Both industrial laboratories had obtained their data using AAS for the elemental determinations, although different dissolution procedures were used. USGS published data are based on average results reported by various laboratories by several

Table 7.—Comparison of interlaboratory analyses of manganese nodule standards

Standard	Micrograms per gram								Weight percent							
	As	Be	Cd	Cr	Pb	Sb	Se	Tl	Ba	Co	Cu	Fe	Mn	Mo	Ni	Zn
A-1:[1]																
Lab A	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.24	0.97	7.3	24.2	ND	1.19	0.10
BOM	ND	ND	ND	ND	ND	ND	ND	ND	ND	.22	1.00	7.0	23.4	ND	1.15	.09
A-2:[1]																
Lab A	ND	ND	ND	ND	ND	ND	ND	ND	ND	.25	1.23	6.4	29.8	ND	1.46	.14
BOM	ND	<20	21	30	490	ND	ND	220	0.14	.25	1.18	6.2	28.4	ND	1.40	.14
A-3:[1]																
Lab A	ND	ND	ND	ND	ND	ND	ND	ND	ND	.24	1.28	5.0	34.0	ND	1.26	.15
BOM	ND	<20	20	30	400	ND	ND	180	.15	.24	1.28	4.8	32.2	ND	1.24	.15
B-1:[1]																
Lab B	ND	2	ND	ND	480	ND	ND	ND	.26	.22	1.01	6.8	26.7	0.05	1.36	.13
BOM	48	3	14	60	450	41	ND	190	.26	.24	1.00	6.4	26.6	.06	1.33	.14
B-2:[1]																
Lab B	ND	2	ND	ND	490	ND	ND	ND	.25	.26	1.30	5.9	31.4	.06	1.55	.18
BOM	73	2	20	50	455	57	ND	230	.25	.25	1.27	5.7	31.8	.05	1.51	.17
USGS A-1:[2]																
USGS	298	6	6.5	24	846	34	ND	61	.17	.31	.11	10.9	18.5	.04	.64	.06
BOM	306	ND	8.0	30	860	25	<0.26	ND	.19	.31	.12	11.3	20.0	ND	.69	.07
USGS P-1:[2]																
USGS	39	3	22	17.5	555	50	ND	154	.34	.22	1.15	5.8	29.1	.08	1.34	.16
BOM	45	4	22	15	495	44	<0.26	150	.31	.24	1.17	6.1	29.9	.07	1.36	.15

BOM Bureau of Mines. ND Not determined. USGS U.S. Geological Survey.

[1] Industrial laboratory in-house reference standard. [2] See reference 11 for information on the USGS reference sample.

Table 8.—Round-robin results for Cuprion process reject waste material, solid phase

Element	Bureau of Mines				Industrial	
	SLCRC	AIRC	RRC	AvRC	Lab B	Lab C
CONCENTRATION, wt pct						
Ba	0.26	0.33	0.54	0.24	0.29	ND
Co	.17	.17	.19	.18	.17	0.18
Cu	.14	.14	.13	.14	.15	.12
Fe	5.5	7.8	4.8	5.8	5.6	6.4
Mn	26.0	27.4	25.8	27.0	27.8	32.2
Ni	.20	.21	.32	.22	.20	.28
Zn	.11	.12	<.01	.13	.11	.11
CONCENTRATION, μg/g						
As	45	46	<40	49	ND	55
Be	ND	ND	2	<3	ND	ND
Cd	40	30	21	20	19	49
Cr	29	56	<500	30	21	ND
Mo	50	ND	28	68	<100	190
Pb	590	650	540	500	600	410
Sb	<10	24	72	40	ND	38
Se	<1	<5	ND	ND	ND	1
Tl	150	<10	ND	83	ND	160

AIRC Albany (OR) Research Center.
AvRC Avondale (MD) Research Center.
ND Not determined.
RRC Reno (NV) Research Center.
SLCRC Salt Lake City (UT) Research Center.

Table 9.—Round-robin results for Cuprion process reject waste material, liquid phase, micrograms per milliliter

Element	Bureau of Mines				Industrial
	SLCRC	AIRC	RRC	AvRC	lab C
As	0.015	0.01	<0.03	0.018	0.025
Ba	.16	.11	.17	<.8	.27
Be	ND	ND	.003	<.03	<.01
Cd	<.01	<.05	<.004	<.03	<.05
Co	<.01	<.1	<.2	<.3	.10
Cr	<.1	.3	<.04	<.2	<.1
Cu	.15	<.10	<.50	<.11	<.05
Fe	<.01	<.20	<.20	<.50	<.05
Mn	<.1	<.1	<.03	<.7	<.02
Mo	14	ND	15	30	63
Ni	<.01	<.10	<.03	<.10	<.20
Pb	<.1	<.5	<.06	<.2	<.01
Sb	<.01	<.01	<.02	.007	<.018
Se	.02	<.02	.16	.02	<.03
Tl	.4	<.1	ND	<.2	.11
Zn	<.1	<.1	3.3	<.03	<.04

AIRC Albany (OR) Research Center.
AvRC Avondale (MD) Research Center.
ND Not determined.
RRC Reno (NV) Research Center.
SLCRC Salt Lake City (UT) Research Center.

methods (*11*). The Avondale results were obtained from the HCl-HF and the HNO_3-HF dissolution procedures. Results obtained by AAS by Avondale personnel agree well with results reported by the industrial laboratories and the USGS.

A reject waste slurry material from the Cuprion process was prepared, blended, and samples were sent to the Bureau's Salt Lake City (UT), Albany (OR), Reno (NV), and Avondale (MD) Research Centers and to two independent industrial laboratories (B and C). Analytical data were requested for the 16 elements of interest, as well as any other element or ionic species they could conveniently determine. Analyses of both the liquid and solid phases were performed by all laboratories except industrial laboratory B, which reported only the solid phase analysis. Table 8 gives the results obtained by the six laboratories for the solid phase. Good agreement was obtained for the major and minor elements; Co, Cu, Ni, and Zn, and the trace elements; As, Be, Cr, Pb, and Se. The elements Ba, Fe, Cd, Mn, Mo, Sb, and Tl had only moderate agreement. It should be noted that the Avondale laboratory and industrial laboratory B have more experience in analyzing nodules and nodule waste materials than the other four laboratories. However, agreement overall can be considered acceptable for this initial round robin.

Table 9 gives the round-robin results for the liquid phase of the tested material. Again agreement for most of the elements provides confidence in the analytical methods used.

The results for both phases of the tested material and the manganese nodule standards indicate that standard dissolution procedures listed in this report for nodules as well as procedures used in laboratories accustomed to analyzing inorganic matrices are adequate for determining the elemental content of nodules and reject waste materials.

LEACHING TESTS

EP TOXICITY TEST

According to EPA regulations under the Resource Conservation and Recovery Act (RCRA) (*31*), a solid waste must be listed as a hazardous waste if it exhibits any of the following characteristics as defined in RCRA: ignitability, corrosivity, reactivity, and/or extraction procedure (EP) toxicity (*8-9*).

Reject waste materials from manganese nodule processing will not exhibit any properties of ignitability or reactivity. Corrosivity applies primarily to liquid wastes and should not be a problem if adequate waste management practices are used in the washing of the tailings.

The only applicable hazardous waste criterion is the EP toxicity test. Briefly, the EP toxicity test consists of agitating, for 24 h, a minimum sample weight of 100 g of filtered material in 1,600 mL of distilled water (maintain a 16:1 water-to-solids ratio for larger sample weights) to which a maximum of 400 mL of 0.5*N* acetic acid (4 mL of acid per gram of material) may be added to maintain a pH of 5.0 ± 0.2. If all 400 mL of the acid is not required to achieve the desired pH, the remaining volume to make 2,000 mL (20:1 liquid-to-solid ratio) is added as distilled water. The solution is filtered on a 0.45-μm pore size filter. The resulting extract (liquid portion) in the EP toxicity test is not to exceed 100 times the National Drinking Water Standard for concentrations of eight metals: Ag, As, Ba, Cd, Cr, Hg, Pb, and Se. The EP toxicity limits, in micrograms per milliliter, are as follows: Ag, 5; As, 5; Ba, 100; Cd, 1; Cr, 5; Hg, 0.2; Pb, 5; and Se, 1.

ASTM SHAKE EXTRACTION TEST

A second leaching test, the American Society for Testing Materials (ASTM) shake extraction test (*2*), has been proposed by ASTM as an alternate method for evaluating wastes, especially those of low organic content such as mining waste.

This test consists of contacting a minimum of 350 g of dried material with distilled deionized water; the weight of water to be four times the sample weight. The slurry is agitated in a closed container for 48 h and the liquid portion filtered on 0.45-μm filter paper. The extract is then analyzed for the desired components including those outlined in the RCRA criteria.

U.S. ARMY CORPS OF ENGINEERS SEAWATER ELUTRIANT TEST

In the possible case of ocean disposal of nodule reject waste materials, either by ocean dumping or by ocean outfalls, a seawater leachate test may provide more appropriate data than the previous two leach tests. The Corps of Engineers dredge material elutriant test can be used to evaluate the extent of seawater-leachable metals in the waste materials (*33*). The procedure consists of mixing a weighed volume of material with four times the volume of seawater, agitating for 1 h, filtering and analyzing the seawater solution. Concentrations are compared with those in the seawater prior to leaching. Based on this analysis, concentrations of the elements at proposed mixing levels found in ocean outfalls or in ocean dumping can be extrapolated. Depending on final regulations in regard to ocean disposal, the degree of mixing required can be regulated by either dumping large amounts at once for minimal mixing rates or by trickling to provide for high mixing rates. NOAA has an ongoing study to establish requirements in this area.

RESULTS OF LEACHING TESTS

The EP toxicity test, the ASTM shake extraction test, and the Corps of Engineers seawater elutriant test were all applied to the Cuprion pilot plant tailings described in table 8. The results are listed in table 10. Comparison of the established

Table 10.—Element concentration in leachate from leaching tests on Cuprion process reject waste material, micrograms per milliliter

Element	EP toxicity test	ASTM shake extraction test	Seawater elutriant test
Ag	<0.07	<0.07	<0.07
As	.004	<.003	<.003
Ba	<2	<2	<2
Be	<.06	<.06	<.06
Cd	.06	<.05	<.05
Co	12	<.3	<.3
Cr	<.4	<.4	<.4
Cu	1.3	<.2	<.2
Fe	<.5	<.5	<.5
Hg	.019	ND	ND
Mn	1,690	<.06	.28
Mo	<.6	3.8	<.6
Ni	9.9	<.1	<.10
Pb	<.7	<.7	<.7
Sb	.003	<.003	<.003
Se	<.003	<.003	<.003
Tl	<2	<2	<2
Zn	2.5	<.02	<.04

ND Not determined.

NOTE.—EP toxicity test has the following maximum allowable concentration of contaminants for 8 elements, in micrograms per milliliter: Ag, 5; As, 5; Ba, 100; Cd, 1; Cr, 5; Hg, 0.2; Pb, 5; and Se, 1.

EP toxicity test limits listed in table 10 with the concentrations leached from the Cuprion pilot plant rejects show that leachate concentrations from this waste material are consistently one to three orders of magnitude lower than would be required to be classified as hazardous. Manganese, cobalt, and nickel were leached from the rejects to some extent by the EP toxicity test but none of these are considered in the hazardous waste criteria.

CONCLUSIONS

In general, the conventional physical and chemical analytical procedures used by laboratories experienced in working with inorganic matrices are applicable to manganese nodules and their processing reject waste materials. The high iron and manganese content of nodule materials must be taken into account in chemical analyses, especially for possible interferences in trace element determinations. The precautions are described or referenced in the text for each of the various methods discussed.

The fine-grained or amorphous nature of manganese nodules and nodule tailings generally limit the identification of mineral compounds to the major and minor constituents such as manganese carbonate or oxide, quartz, feldspars, and clays. The use of referenced electron microscopic techniques is purported to identify minerals in concentrations less than about 5 wt pct. The iron compounds are often amorphous, requiring the use of referenced infrared spectroscopy or chemical methods for identification.

In comparisons of leachate tests on Cuprion pilot-plant tailings, the EP toxicity test seemed to show greater leaching ability for the eight regulated elements than the ASTM shake extraction test or the Corps of Engineers seawater elutriant test. However, these levels were one to three orders of magnitude lower than would be required for the wastes to be classified as hazardous. Three elements not listed in classifying a waste as hazardous, Mn, Co, and Ni, showed some leachability, but the leaching was minimal.

The procedures described in this report are not being suggested as standard methods, but are simply a review of state-of-the-science analytical techniques as applied to manganese nodule materials. Any skilled inorganic analyst taking the precautions described in this report for the interferences should be capable of providing reliable analyses of manganese nodules and nodule processing reject waste materials.

REFERENCES

1. Allen, T. Particle Size Measurement. Chapman & Hall, 1975, pp. 301-312.

2. American Society for Testing and Materials. D3987-81 in Annual Book of Standards, Part 31: Water Standard Test Method for Shake Extraction of Solid Waste With Water. Philadelphia, PA, 1982, 5 pp.

3. _____. Annual Book of Standards, Part 19: Natural Building Stones; Soil and Rock; Peats, Mosses and Humus. Philadelphia, PA, 1977, 494 pp.

4. Bertin, E. P. Principles and Practice of X-Ray Spectrometric Analysis. Plenum, 1970, 679 pp.

5. Brunfelt, A. O., and E. Steinnes. A Neutron-Activation Scheme Developed for the Determination of 42 Elements in Lunar Material. Talanta, v. 18., 1971, pp. 1197-1208.

6. Busch, R. A., R. R. Backer, L. A. Atkins, and C. D. Kealy. Physical Property Data on Fine Coal Refuse. BuMines RI 8062, 1975, 40 pp.

7. Dames & Moore and EIC Corporation. Description of Manganese Nodule Processing Activities for Environmental Studies, Vol. III. Processing Systems Technical Analysis. U.S. Dep. of Commerce-NOAA, Office of Marine Minerals, Rockville, Md., 1977, 540 pp.; NTIS PB 274915.

8. Federal Register. Part IV, Environmental Protection Agency: Hazardous Waste; Proposed Guidelines and Regulations and Proposal on the Identification and Listing. V. 43, No. 243, Dec. 18, 1978, pp. 58946-59028; 110-CFR, Part 250.

9. _____. Parts II-IX, Environmental Protection Agency: Hazardous Waste and Consolidated Permit Regulations. V. 115, No. 98, May 19, 1980, Book 2, pp. 33063-33285; 110-CFR, Parts 260-265.

10. Fewkes, R. H., W. D. McFarland, W. R. Reinhart, and R. K. Sorem. Evaluation of Metal Resources at and Near Proposed Deep Sea Mine Sites (grant G0284008, WA State Univ.). BuMines OFR 108-80, 1980, 242 pp.; NTIS PB 80-228992.

11. Flanagan, F. J., and D. Gottfried. USGS Rock Standards, III: Manganese Nodule Reference Samples USGS-Nod-A-1 and USGS-Nod-P-1. U.S. Geol. Surv. Prof. Paper 1155, 1980, 39 pp.

12. Frazer, J. Z., M. B. Fisk, J. Elliot, M. White, and L. Wilson. Availability of Copper, Nickel, Cobalt, and Manganese From Ocean Ferromanganese Nodules (grant G0264024, Scripps Inst. Oceanography). BuMines OFR 121-79, 1978, 141 pp.; NTIS PB 300 356.

13. Haynes, B. W. Electrothermal Atomic Absorption Determination of Arsenic and Antimony in Combustible Municipal Solid Waste. At. Absorp. Newsl., v. 17, No. 3, 1978, pp. 49-52.

14. Haynes, B. W., G. W. Kramer, and J. A. Jolly. Fluorine and Uranium in Phosphate Rock Processing and Waste Materials. BuMines RI 8576, 1981, 17 pp.

15. Haynes, B. W., and S. L. Law. Predicted Characteristics of Waste Materials From the Processing of Manganese Nodules. BuMines IC 8904, 1982, 10 pp.

16. Haynes, B. W., S. L. Law, and D. C. Barron. Mineralogical and Elemental Description of Pacific Manganese Nodules. BuMines IC 8906, 1982, 60 pp.

17. Haynes, B. W., S. L. Law, and R. Maeda. Updated Process Flowsheets for Manganese Nodule Processing. BuMines IC 8924, 1983, 100 pp.

18. Koch, R. C. Activation and Analysis Handbook. Academic, 1960, 219 pp.

19. Koizuma, H., and K. Yasuda. New Zeeman Method for Atomic Absorption Spectrophotometry. Anal. Chem. v. 47, 1975, pp. 1679-1682.

20. Kramer, G. W., and B. W. Haynes. Anion Characterization of Florida Phosphate Rock Mining Materials and U.S. Cement Kiln Dust by Ion Chromatography. BuMines RI 8661, 1982, 8 pp.

21. Manning, D. C. Spectral Interferences in Graphite Furnace Atomic Absorption Spectroscopy I. The Determination of Selenium in an Iron Matrix. At. Absorp. Newsl, v. 17, No. 5, 1978, pp. 107-108.

22. Potter, R. M., and G. R. Rossman. The Tetravalent Manganese Oxide: Identification, Hydration, and Structural Relationships by Infrared Spectroscopy. Am. Mineral., v. 64, 1979, pp. 1199-1218.

23. _____.Mineralogy of Manganese Dendrites and Coatings. Am. Mineral., v. 64, 1979, pp. 1219-1226.

24. Price W. J. Analytical Atomic Absorption Spectrometry. Heyden, 1974, p. 80.

25. Ricci, E., and F. F. Dyer. Second Order Interference in Activation Analysis. Nucleonics, v. 22, No. 6, 1964, pp. 45-50.

26. Sawicki, E., J. D. Mulik, and E. Wittgenstein. Analysis of Industrial Wastestreams. Dionex Corp. (Sunnyvale, CA) Applications Note No. 11, August 1978, 2 pp.

27. _____. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor Sci., v. 1 and 2, 1978, 645 pp.

28. Sighinolfi, G. P., and C. Gorgoni. AA Spectrochemical Analysis for Ultra Trace Elements in Geological Materials by Hydride-Forming Techniques: Selenium. Talanta, v. 28, 1981, pp. 169-172.

29. Small, H., T. S. Stevens, and W. C. Bauman. Novel Ion Exchange Chromatographic Methods Using Conductimetric Detection. Anal. Chem., v. 47, 1975, pp. 1801-1809.

30. Turner, S., M. D. Siegel, and P. R. Buseck. Structural Features of Todorokite Intergrowths in Manganese Nodules. Nature, v. 296, 1982, pp. 841-842.

31. U.S. Congress. Resource Conservation and Recovery Act of 1976. Public Law 94-580, Oct. 21, 1976.

32. U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA-600/4-79-020, March 1979, 460 pp.

33. U.S. Environmental Protection Agency and U.S. Army Corps of Engineers. Ecological Evaluation of Proposed Discharge of Dredged Material Into Ocean Waters. Environmental Effects Laboratory, Waterways Experiment Station, U.S. Army Corps of Engineers, Vicksburg, MS, July 1977, 103 pp.

☆U.S. GOVERNMENT PRINTING OFFICE: 1983-605-015/63

INT.-BU.OF MINES,PGH.,PA. 27144

THE LIBRARY OF CONGRESS

THE LIBRARY OF CONGRESS

WERT
BOOKBINDING
MIDDLETOWN, PA.
FEB. 34
We're Quality Bound

LIBRARY OF CONGRESS
0 002 959 882 4